1.Photocopying Entangled Region
2. Oligomeric Photoinitiators

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RR 03/09/00

Lecture Notes

Radical Photocopying Experiment

Timing Diagram

Dual Detector GPC setup

Labeled "photocopied"

polymer

Monomeric

compouns

Fluorescence GPC Trace: Detects only Living chains

Elution time

Detecting naphthyl moieties only with 300 nm excitation

and 350 nm emission

Number of labeled chains proportional to the integrated area

mol. weight increase

Photocopying the Entangled Region

Below 0.4 % non-entangled region

Less than 2 min polymerization time and 0.14 wt. % AIBN

AIBN; solid circles 0.3 wt. %, open circles 0.5 wt.%

Linear regime below ca. 15 min and autoacceleration after (RI data)

(ca. 40% conversion)

Efficiency of photolabeling becomes progressively more difficult

with conversion

no labeled polymer in the absence of light

~ 90%

~ 90%

~ 40%

Chain Length as a Function of Conversion

Dead chains

Dead chains

Persistent Radical Effect in FRP of MMA

ESR signal starts to appear 20 minutes after initiation at 90 °C:

at high conversions only (> ca. 90%)

" 9 line spectrum"

Literature Controversy in the Assignments PMMA. Spectra

" 9 line spectrum: high conversions"

" 13 line spectrum: low conversions"

ESACURE **KIP 150**

ESACURE KIP 100F

ESACURE KTO 46

2. Oligomeric Photoinitiators:

Good Models (?) for End Labeled Polymers

CIDEP Quenching with Methylmetacrylate

RI - GPC of the Oligomeric Photoinitiators

Mn = 800, PD 1.03

Mn < 500

All samples are essentially mixtures of trimers and tetramers

Esacure **KIP 150**

all oligomers are brown tars but sufficiently soluble in CH3CN and THF

Esacure **KIP 150**

50 - 350 ns

TR ESR of Esacure **KIP 150** in MeCN

400 - 1100 ns

Benzyl line is the most intense one

Model Compound Darocure 1173

50 - 350 ns

400 - 1100 ns

Benzyl line is weaker now: could it be the sign of lower mobility of

benzyl radical in oligomer compared to monomer (Darocure 1173) ?

ESACURE KIP 100F

50 - 350 ns

400 - 1100 ns

Conclusions

Photocopying technique can be applied to analysis of high conversion FRP

Thermal initiation of polymerization by DNS is negligible even at 90 °C

- Efficiency of photolabeling appears to decrease with conversion

Oligomeric photoinitiators appear to to produce CIDEP through the similar

mechanism as monomers (RPM)

Future Directions

Dead polymer (monodisperse) effect on the quality of the photocopy

CIDEP of end-labeled photoinitiators